Modulated Cr(III) Oxidation in KOH Solutions at a Gold Electrode: Competition between Disproportionation and Stepwise Electron Transfer

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Abstract The electrochemical oxidation of aqueous Cr(III) was examined using cyclic voltammetry with a polycrystalline Au electrode in KOH solutions of varying pH and Cr(III) concentration. The mechanism and kinetics for the oxidation of Cr(III) is a quasi-reversible diffusion-controlled reaction and is largely dependent on the solution pH. The reaction mechanism is initiated by an irreversible electrochemical electron transfer to form Cr(IV) which is the rate-determining step (RDS). Following the RDS, subsequent oxidation of Cr to its hexavalent state occurs by the disproportionation of Cr(IV) at low KOH concentrations and electron transfer at high KOH concentrations due to the involvement of OH^- in the disproportionation reaction. As the solution pH increases, the Cr(III) oxidation peak potential shifts negatively owing to the involvement of OH^- in the RDS. The competitive adsorption of OH^- and CrO_2^- on the electrode surface also plays an important role in the oxidation behavior.

Keywords: Cr(III) oxidation; KOH; Mechanism transition; pH dependent; Competitive adsorption

1. Introduction

Due to the wide application in geochemistry[1], environmental treatments[2] and industrial processes[3], considerable efforts have been conducted on the redox cycling of chromium compounds in soils and aquatic environments over recent years. Chromium is mainly present in two stable oxidation states, trivalent and hexavalent[4].

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Trivalent chromium is considered relatively harmless and even a trace nutrient for mammals[5], but the low solubility of Cr(III) compounds, especially oxides and hydroxides, are likely to be the major limitation to their mobility in aquatic environments[6]. In contrast, hexavalent chromium compounds, which are very soluble and consequently mobile in groundwater[3], are considered to be extremely toxic and carcinogenic[7]. Most previous studies have been focused on the reduction of Cr(VI) to Cr(III) owing to its significant environmental concern[8-10]. Recently, due to the importance in mineral processing, solid waste treatment and pharmaceutical analysis, mechanistic investigations for the oxidation of Cr(III) have gained particular impetus[11-13].

The oxidation of Cr(III) compounds is strongly influenced by the reaction media, especially pH[14]. In acidic media, and based on XPS analysis, Banerjee[15] proposed the consecutive three step mechanisms involving Cr(IV) and Cr(V) as intermediates during the oxidation of aqueous Cr^{3+} at bimessite (MnOOH) surfaces. Silvester[16] postulated that the origin of Cr(IV) and Cr(V) compounds in the Cr(III)-$MnO_{1.75}$ system was not only controlled by reaction at the mineral surface, but also the disproportionation of these intermediates in the aqueous phase. However, under alkaline conditions, the mechanism for oxidation of Cr(III) compounds appears to be significantly different. Zhao[17] investigated the aqueous Cr(III) oxidation by the hydroxyl radical in NaOH solution and found that the formation of Cr(VI) is from the disproportionation of Cr(IV)-bearing dimer. Friese[18] discovered that there is a mechanism transition for the Cr(III) oxidation by peroxydisulfate due to the media

alkalinity, and the Cr(V) intermediate could not be detected, possibly due to its very short lifetime. Obviously, the Cr(III) oxidation mechanism is substantially affected by solution pH, and the reaction usually includes the intermediates of Cr(IV) and Cr(V) in acidic solution, while in alkaline solution it appears that only Cr(IV) is involved.

Besides, the pH-dependent Cr(III) speciation is closely related to its oxidation behavior[19, 20]. Although the chromium-water system is very complex and some discrepancy still exists on the Cr speciation, it is generally accepted that the transition between different Cr species takes place in a narrow pH range[20]. Cr(III) and Cr(VI) are present as different forms depending on pH, and these species possess different redox stabilities, leading to the different oxidation nature of Cr(III)[20]. In addition, the Cr(III) mobility is significantly affected by the environment, especially the pH condition in both solid phase and aqueous solution, and consequently the Cr(III) oxidation mechanisms varies[19, 21, 22]. Chinthamreddy[23] attributed the low extent of Cr(III) oxidation in manganese-enriched glacial till to the initial precipitation of $Cr(OH)_3$ due to the high pH of the soil. Skoluda[24] studied the electrochemical oxidation of Cr(III) at different single crystal gold electrodes, and identified that the electrode surface structure effect originates from the competitive adsorption between OH^- and CrO_2^- at the electrode surfaces.

It is obvious that Cr(III) oxidation can be manipulated by adjusting the pH of the reaction media. Welch[25] investigated the electrochemical oxidation of Cr(III) compounds (0.1 mM to 1 mM) in KOH solution (0.1 and 1.0 M) using a polycrystalline Au electrode and discovered the involvement of OH^- ions in this

multi-step reaction. It is proposed that the pathway for the electrochemical oxidation of Cr(III) is composed of the first rate-determining electron transfer and subsequent diproportionation or further two fast electron transfer reactions as follows:

$$CrO_2^- + OH^- \rightarrow e^- + H^+ + CrO_3^{2-} \quad (1)$$

$$CrO_3^{2-} \rightarrow e^- + CrO_3^- \quad (2)$$

$$CrO_3^- + OH^- \rightarrow e^- + H^+ + CrO_4^{2-} \quad (3)$$

However, due to the complexity of this system, the mechanism and kinetics of Cr(III) electro-oxidation in alkaline solution are still not fully understood. Therefore, in order to obtain further information regarding the oxidation behavior and elucidate the effect of media pH on the Cr(III) oxidation mechanism, the electrochemical oxidation behavior of Cr(III) compounds in KOH solutions with concentration ranging from 0.1 M to 3.0 M was investigated in this study by means of cyclic voltammetry.

2. Experimental Section:

2.1 Chemicals and Solutions

KOH pellets (p.a. grade, Merck) and $Cr(NO_3)_3$ (99.99 %, Sigma-Aldrich) were used without further purification. All solutions were prepared from Millipore Milli-Q water (18 MΩ cm). Before each experiment, the test solution was degassed with ultra-pure nitrogen and then maintain under a nitrogen atmosphere.

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2.2 Instrumentation

Experiments were conducted in a standard 150 mL three-electrode electrochemical cell at 25±0.2 ^{o}C with an electrochemical workstation (PCI4G750, Gamry) by employing cyclic voltammetry (CV). A gold (99.99% purity, polycrystalline, 0.23 cm^2 effective area) cylinder electrode was used as the working electrode. A large-area Pt foil served as the counter electrode. All potentials were measured and reported versus a saturated calomel electrode (SCE).

Prior to each measurement, the working electrode was polished with decreasing grades of aluminia (1.0 to 0.3μm) to achieve a mirror-like surface, then it was sonicated and washed in purified water to remove traces of aluminia. After that, the working electrode was electrochemically pretreated by cycling between the onset potential of H_2 and O_2 evolution reactions in the corresponding KOH solution until reproducible and well-defined cyclic voltammetry curves were obtained and the final potential was stopped at the onset of H_2 evolution.

3. Results and Discussion:

3.1 Identification of the Chemical Step in the Electro-oxidation of Cr(III)

The electrochemical oxidation of Cr(III) was investigated at polycrystalline gold electrode in KOH solutions in an electrochemically active region (pH > 12)[25]. The

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trivalent Cr occurs as CrO_2^- in this pH region[26]. Figure 1 shows the cycle voltammetry (CV) response of 0.50 mM Cr(III) and its corresponding blank curve in 0.1 M KOH solution at 200 mV/s. As can be seen in the blank solution curve, the formation of gold(I) oxide and gold(III) oxide are observed at -0.08 V and 0.35 V, respectively, and their corresponding reduction peaks emerge at -0.18 V and 0.06 V, respectively[27]. Moreover, formation of $Au(OH)^-$ species, which is the surface active species for Cr(III) oxidation, occurs over a wide potential range via different pathways as follows[25]:

-0.44 V<E< -0.04 V $\quad Au + OH^- \rightarrow Au(OH)^-_{ads}$ (4)

E> -0.04 V $\quad Au + OH^- - e^- \leftrightarrow Au(OH)^-_{ads}$ (5)

Clearly, the later reaction via electron transfer occurs around the same position as formation of the gold(III) oxide reaction and thus experimentally appears as a pair of single peaks. In the presence of trivalent chromium, the oxidation peak at 0.08 V is attributed to the Cr(III) oxidation, and there is no corresponding reduction peak, indicating an pseudo-irreversible reaction. It should be noted that the increase in the oxidation peak at 0.35 V stems from the "tail" effect of the Cr(III) oxidation peak and not increased gold oxide formation. The peak current for the gold surface reactions decreases due to the passivation effect of chromium[28]. The passivating effect is observed by the decreased reduction peak current in the presence of chromium at 0.06 V.

The effect of the Cr(III) concentration on oxidation behavior was measured in a wide range of 0.15 mM to 3.00 mM and illustrated in Fig 2a. The increase of peak current is linearly proportional to the Cr(III) concentration in the range of 0.15 mM to

1.10 mM as shown in Fig 2b and the peak potential of Cr(III) remains constant at 0.08 V in this region, indicating first order kinetics which is consistent with results from the previous study[25] for the region between 0.1 mM and 1 mM. However, at Cr(III) concentrations above 1.80 mM, the peak potential (E_{pa}) for Cr(III) oxidation monotonically shifts positively and the corresponding peak current appears below the first order relationship with respect to the Cr(III) concentration as shown in Fig 2b.

As the Cr(III) concentration increases, the peak current for gold surface reactions decreases due to the passivation. Interestingly, as the Cr(III) concentration increases to 1.10 mM, the reduction peak at 0.06 V breaks into two peaks at 0.05 V and 0.12 V, respectively. With a further increase in Cr(III), the reduction peak at 0.05 V decreases more significantly than the reduction peak at 0.12 V. It is believed this phenomenon stems from the competitive adsorption between OH^- and CrO_2^- [24]. As CrO_2^- increases, the OH^-–bearing surface reactions are greatly inhibited and consequently the previous one reduction peak breaks into two peaks. The peak at 0.05 V is for the OH^- desorption reaction and the other peak at 0.12 V corresponds to the gold(III) oxide reduction. The OH^-_{ads} is an important reaction intermediate for Cr(III) oxidation[25], thus with the further increase of CrO_2^-, its blocking effect leads to the shifts noted in peak potential(E_{pa}) and peak current(i_{pa}) for Cr(III) oxidation.

Further, as the Cr(III) concentration increases, another new reduction peak emerges at -0.75 V, this peak is attributed to the corresponding Cr(VI) reduction[29]. As shown in Fig 2c, there is a linear relationship between the peak current ratio (i_{pc}/i_{pa}) for the Cr(III)/(VI) couple and the log(Cr). This Cr(III) concentration-dependent

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irreversibility suggests the involvement of a chemical step. Moreover, the existence of Cr(VI) reduction peak indicates that the chemical reaction is following the irreversible electron transfer mentioned above, which will be further discussed in the following sections.

In order to gain more insight on the mechanism and kinetics, CV curves of 1.5 mM Cr(III) in 0.1 M KOH solution were determined at different scan rates. These are illustrated in Fig 3a. The peak current was found to be linear with the square root of scan rate (25 mV/s to 400 mV/s) as shown in Fig 3b, suggesting kinetics are diffusion controlled. This behavior is also observed in other KOH solutions in this study.

The initial part of the Cr(III) oxidation curve at a scan rate of 200 mV/s is presented in Fig 3c. The oxidation exhibits a good Tafel behavior and as such it can be used to gain information about the rate-determining step (RDS) by calculating the Tafel slope. A slope of 153 mV decade^{-1} is observed ($E_a = 0.153 \times \log(i_a) + 0.109$, $R^2 = 0.99$, 27 points).

From the Tafel slope, the transfer coefficient can be calculated from:

$$b = \frac{2.303RT}{(1-\alpha)F} \tag{6}$$

where b is the slope of the potential against log(i), α the transfer coefficient, R is the gas constant, T is temperature and F is Faraday's constant. From the slope, a transfer coefficient of 0.62 was calculated. This value suggests the rate-determining step is the first electrochemically irreversible electron transfer rather than the coupled chemical step mentioned above, which is consistent with a previous study[25].

For further mechanistic insight, oxidation peak potential is plotted versus the log of

the scan rate in Fig. 3d. According to the multistep electron transfer theory[30], the slope from such a plot can be used to determine the reaction mechanism. A reaction involving no chemical reaction and where the RDS is the first electron transfer, the E_p would positively shift (for an oxidation process) by 30/α mV per decade of scan rate. While slopes of 60/n or 30/n mV per decade of scan rate (n is the number of the electron transfer in successive steps) are expected for charge transfer followed by a reversible or irreversible chemical reaction, respectively. Experimentally, a slope of 19 mV was obtained ($E_{pa} = 0.019 \times \log(v) + 0.09$, $R^2 = 0.98$, 7 points) which is very close to the 20 mV expected for a reaction involving charge transfer followed by a reversible chemical reaction for this three-electron process.

Consequently, based upon the identification of reaction steps in this and previous studies[16, 25], the Cr(III) oxidation mechanism in 0.1 M KOH solution is as follows:

$$CrO_2^- + OH^- \rightarrow e^- + H^+ + CrO_3^{2-} \quad (1)$$

$$2Cr^{IV} \leftrightarrow Cr^{III} + Cr^{V} \quad (7)$$

$$Cr^{IV} + Cr^{V} \leftrightarrow Cr^{III} + Cr^{VI} \quad (8)$$

from which equations (7) and (8) are generally taken to give an overall reaction as follows:

$$3Cr^{IV} \leftrightarrow 2Cr^{III} + Cr^{VI} \quad (9)$$

The electro-oxidation is initiated by an electrochemically irreversible reaction which is the rate-determining step with first order kinetics, followed by the relatively fast disproportionation reaction which leads to the formation of Cr(VI). Its corresponding reduction, including the influence of pH, will be discussed in the following section.

3.2 The Effect of pH on the Electro-oxidation Behavior

In the previous study[25], the oxidation behavior was investigated in 0.1 M and 1.0 M KOH solution to determine the number of protons in the rate-determining step as illustrated in equation (1). In order to obtain the effect of pH on the electro-oxidation mechanisms and kinetics of Cr(III) in KOH solutions, the CV curves in different concentrations of KOH (0.1 M to 3.0 M) were recorded. The Cr(III) concentration was set to 0.5 mM to eliminate the influence of competitive adsorption mention previously. As can be seen in Fig 4, with increasing KOH concentration, the Cr(III) oxidation gradually transfers from an pseudo-irreversible reaction to a quasi-reversible reaction with corresponding reduction peak, although the large peak separation suggests a relatively slow electron transfer. Obviously, the Cr(III) oxidation behavior is strongly affected by pH, and the disproportionation step may be replaced by further electron transfer.

The dependence of diagnostic parameters on pH are summarized in Table 1 and illustrated in Fig 5. The pH values are obtained by employing the activity coefficient data of KOH solutions[31]. It should be noted that the difference of peak currents in different KOH solutions are relatively small, thus the scan rate was set at 200 mV/s to better examine the experimental data. It can be seen that with increasing pH, the Cr(III) oxidation peak current increases and the peak separation decreases. This indicates the facilitating effect of pH on reaction kinetics possibly due to a transition

in the reduction mechanism. More importantly, as the pH increases, the peak potential for Cr(III) oxidation monotonically shifts negatively and there is a linear relationship between the E_{pa} and calculated pH ($E_{pa} = -0.083 \times pH_{cal} + 1.207$, $R^2 = 0.99$, 10 points), suggesting the involvement of hydroxide ion in the reaction. The number of OH^- ions participating in the RDS can be determined using the following equation:

$$\frac{\partial E_{pa}}{\partial pH_{cal}} = \frac{2.303mRT}{\alpha F} \quad (10)$$

where m is the number of OH^- ions to be estimated. It is worth noting that it is nearly constant at 0.62 in a wide pH region, but as the pH increases above 1 M KOH, α significantly increases to 0.75, suggesting a change in reaction mechanism probably has occurred. From this analysis, the number of OH^- ions involved in the RDS was determined to be 1, which agrees well with the proposed scheme shown in equation (1).

The peak current ratio (i_{pc}/i_{pa}) is seen to increase with an increase in pH, suggesting the chemical step is dependent on the media pH, which will be further discussed in the following section. Consequently, there appears to be a pH-dependent mechanism transition, which leads to an increase in reversibility.

3.3 Inhibition of the Disproportionation Step

The Cr(III) concentration-dependent oxidation behavior in 2.0 M KOH solution was measured and presented in Fig 6 to elucidate the pH effect on the disproportionation step. As compared to the CV scans in 0.1 M KOH, the OH^- desorption peak at 0.02 V

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appears at higher Cr(III) concentration in Fig 6a, further confirming that the appearance of this reduction peak reveals the competitive adsorption between OH^- and CrO_2^-. Consequently, the reaction exhibits first order kinetics in a relatively wider Cr(III) concentration region as shown in Fig 6b, than at the lower KOH concentration. Well-defined Cr(VI) reduction peaks are also observed. There is still a large peak separation and the peak current for oxidation is larger than ones at low pH, indicating the pH effect on both the reaction thermodynamics and kinetics.

It is worth noting that with increasing alkalinity, the diffusion properties of electroactive species are suppressed due to increasing viscosity, and thus the diffusion controlled peak current should be reduced[32]. Therefore, the increases in reversibility and peak current suggest a mechanism transition probably has occurred due to increasing pH.

To examine the influence of pH on the chemical step, the dependence of the peak current ratio on the Cr(III) concentration is presented in 0.1 M, 2.0 M and 3.0 M KOH solutions as shown Fig 6c. The i_{pc}/i_{pa} at different KOH solutions both exhibit a linear relationship with the log(Cr) in 0.1 M and 2.0 M KOH solutions, suggesting the existence of a disproportionation reaction. However, the peak current ratio in 2.0 M KOH solution is much higher than the corresponding ratio in 0.1 M, and the slope of i_{pc}/i_{pa} against log(Cr) in 2.0 M is lower. These results indicate the inhibition of disproportionation at high pH. With a further increase in the pH, the values of i_{pc}/i_{pa} increases to 0.144 in 3.0 M KOH and is independent of Cr(III) concentration, suggesting the elimination of disproportionation as part of the electro-oxidation

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mechanism, which will be further discussed in the following section.

According to previous studies[33-36], as the pH increases, the disproportionation of Cr(IV) is hindered, and the Cr(V) intermediate becomes increasingly difficult to be detected. Therefore, the disproportionation reactions involved in the electro-oxidation of Cr(III) in KOH solutions can be expressed as follows:

$$2CrO_3^{2-} + H_2O \leftrightarrow CrO_2^- + CrO_3^- + 2OH^- \quad (11)$$

$$CrO_3^{2-} + CrO_3^- \leftrightarrow CrO_2^- + CrO_4^{2-} \quad (12)$$

which can be given in an overall reaction as follows:

$$3CrO_3^{2-} + H_2O \leftrightarrow 2CrO_2^- + CrO_4^{2-} + 2OH^- \quad (13)$$

With an increase in the solution pH, the Cr(IV) disproportionation is suppressed due to the involvement of OH^-, and the Cr(V) disproportionation is relatively fast, leading to a short lifetime. Consequently, the mechanism of Cr(III) electro-oxidation ranging from 0.1 M to 2.0 M KOH solutions is an electrochemically irreversible electron transfer followed by the pH-dependent Cr(IV) disproportionation as shown in equations (1) and (12).

3.4 Diagnosis of the Oxidation Mechanism in Concentrated KOH solutions

As mentioned previously, at high pH, the disproportionation step is hindered and the transfer coefficient significantly increases. This indicates a transition in reaction mechanism at very high pH. Consequently, the mechanistic parameters for the Cr(III) electrochemical oxidation in 3.0 M KOH solution as a function of Cr(III)

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concentration and scan rate were determined. The peak current ratio of i_{pc}/i_{pa} (scan rate=200 mV/s) is constant at 0.144 ranging from 0.1 mM to 3.0 mM Cr(III), suggesting the elimination of the disproportionation reaction in Fig. 6c. Characterization of the chemical reaction coupled to charge transfers[37] can be determined from the dependence of $i_p/(v^{1/2})$ on v which is illustrated in Fig 7. Clearly, over the entire range of scan rates, the quantity of peak current function is a constant value, indicating the system at 3.0M KOH involves only multistep charge transfers.

Obviously, the trivalent Cr electro-oxidation at this pH (3.0 M KOH) involves a multi-electron-transfer reaction. In considering the reduction sequence for this oxidation, we assume that the three electrons are transferred in sequential one-electron steps (an EEE mechanism) rather than in a simultaneous multi-electron step, since the former nature is generally assumed[38].

The multi-electron transfer process has long been recognized as difficult to decompose into elementary parts, due to the fact that each electron-transfer reaction has its own E^o, k_s, and α values. As for this system, although the reaction is not strictly irreversible, the large peak separation indicates a rate-determining step involvement. Consequently, these results provide an opportunity for analysis of the stepwise reactions. Two limiting cases may be considered – e.g. the first electron transfer is the RDS or not. If the first electron transfer is the RDS, then a slope value of 30 mV/α for the anodic peak potential against the log scan rate should be observed. If it is not, then a slope of 30 mV/(1+α) is expected[39]. The experimental value of 38 mV (E_{pa}= 0.038 × log(v) - 0.018, R^2= 0.98, 7 points) in Fig 8 is close to that predicted, 40 mV,

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(α=0.75) for the $E_{irrev}E_{rev}E_{rev}$ mechanism, indicating the first irreversible electron transfer is the rate-determining step. This is consistent with the previous calculated results as shown in expressions (1) to (3)[25].

Finally, the disproportionation step for Cr(III) electro-oxidation in 3.0 M KOH solution was eliminated due to the high pH. This process is determined to be a stepwise three-electron-transfer process in which the first electron transfer is the RDS and accounts for the pH-dependent peak current increase and the favored reversibility mentioned above.

4. Conclusions.

In this paper, the oxidation of Cr(III)at a polycrystalline gold electrode has been investigated over a wide range of KOH (0.1 to 3.0 M) and Cr(III) (0.5 to 3.0 mM) concentrations using cyclic voltammetry. It is observed that the oxidation behavior is substantially affected by the media pH and there is a pH-modulated mechanism transition from an EC (electron transfer - disproportionation) reaction at low KOH concentrations to the stepwise three-electron-transfer process at high KOH.

The electro-oxidation of Cr(III) is attributed to a quasi-reversible diffusion-controlled reaction. It is initiated by an electrochemical irreversible electron transfer which is the rate-determining step, and it is followed by the reversible disproportionation of Cr(IV) in dilute KOH solution. However, due to the involvement of OH^- in the disproportionation reaction, the mechanism transfers to a

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stepwise three-electron-transfer process in which the first irreversible electron transfer is followed by fast two-electron transfers in concentrated KOH solution. This change in mechanism favors the oxidation thermodynamics and kinetics. As the solution pH increases, the Cr(III) oxidation peak potential shifts negatively owing to the involvement of OH^- in the RDS. The competitive adsorption between OH^- and CrO_2^- on the electrode surface also plays an important role in the oxidation behavior.

In summary, it is concluded that the Cr(III) electrochemical oxidation is significantly affected by KOH concentration. This pH effect, which influences the oxidation mechanism and kinetics, arises from the diffusion properties of Cr(III) as affected by pH and the involvement of the OH^- ion in the reaction steps.

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Captions for figures and tables

Fig 1. Cyclic voltammograms of gold in the presence(red) and absence(black) of 0.5 mM Cr(III) in 0.1 M KOH solution at a gold electrode, scan rate=200 mV/s.

Fig 2. The effect of Cr(III) concentration on the oxidation behavior in 0.1 M KOH solution at a gold electrode: (a) comparison of the CV curves at 0.50, 1.10, 2.00 and 3.00 mM Cr(III) concentration, (b) a plot of oxidation peak current vs. Cr(III) concentration, (c) variation of peak current ratio (i_{pc}/i_{pa}) as function of log(Cr). Scan rate=200 mV/s.

Fig 3. Cr(III) oxidation behavior as function of scan rate in 1.5 mM Cr(III), 0.1 M KOH solution at a gold electrode: (a) cyclic voltammograms with increasing scan rates(50-300 mV/s), (b) variation of Cr(III) oxidation peak current as function of square root of scan rate(25-400 mV/s), (c) Tafel slope of the Cr(III) oxidation at scan rate of 200 mV/s, (d) a plot of anodic peak potential E_{pa} vs. log v(25- 400 mV/s).

Fig 4. The effect of KOH concentration (0.1, 1.0 and 3.0 M) on cyclic voltammograms measured in 0.5 mM Cr(III) using a polycrystalline a gold electrode. Scan rate=200 mV/s.

Fig 5. The dependence of (a) Cr(III) oxidation peak current on the KOH concentration,

(b) oxidation peak potential and (c) peak current ratio on the pH during the 0.5 mM Cr(III) electro-oxidation in KOH solutions at a gold electrode, scan rate=200 mV/s.

Fig 6. Electrochemical behavior of Cr as function of Cr(III) concentration in 2.0 M KOH solutions at a gold electrode: (a) comparison of CV curves at 0.50, 1.10, 2.00 and 3.00 mM Cr(III), (b) variation of oxidation peak current as function of Cr(III) concentration, (c) variation of peak current ratio (i_{pc}/i_{pa}) as function of log (Cr) in 0.1 M, 2.0 M and 3.0 M KOH solutions. Scan rate=200 mV/s

Fig 7. The dependence of peak current function on the scan rate (25 mV/s to 2 V/s) of 1.5 mM Cr(III) electro-oxidation in 3.0 M KOH solutions at a gold electrode.

Fig 8. The plot of anodic peak potential against log scan rate (25 mV/s to 400 mV/s) for the 1.5 mM Cr(III) electro-oxidation in 3.0 M KOH solutions at a gold electrode.

Table 1. The pH-dependent diagnostic parameters of 0.5 mM Cr(III) electro-oxidation in KOH solution at a gold electrode, scan rate=200 mV/s.

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Table 1.

C_{KOH}/M	pH_{cal} [a]	E_{pa}/V	i_{pa}/μA	E_{pc}/V	i_{pc}/μA	ΔE_p/V	i_{pc}/i_{pa}	α
0.1	12.90	0.085	157	-	-	-	-	0.62
0.2	13.18	0.060	163	-	-	-	-	0.63
0.3	13.34	0.051	170	broad	-	-	-	0.61
0.5	13.56	0.031	177	broad	-	-	-	0.62
0.8	13.77	0.010	186	-0.600	19	0.610	0.105	0.63
1.0	13.87	0.005	195	-0.602	21	0.607	0.110	0.63
1.5	14.09	-0.016	204	-0.610	23	0.594	0.115	0.66
2.0	14.25	-0.028	207	-0.612	25	0.584	0.120	0.68
2.5	14.39	-0.039	210	-0.614	29	0.575	0.138	0.72
3.0	14.51	-0.046	212	-0.616	31	0.570	0.144	0.75

[a] The pH values were calculated using the activity coefficient data from Robinson[31]

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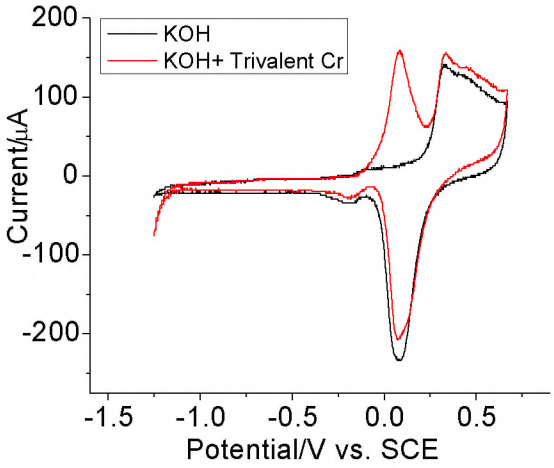
Fig 1.



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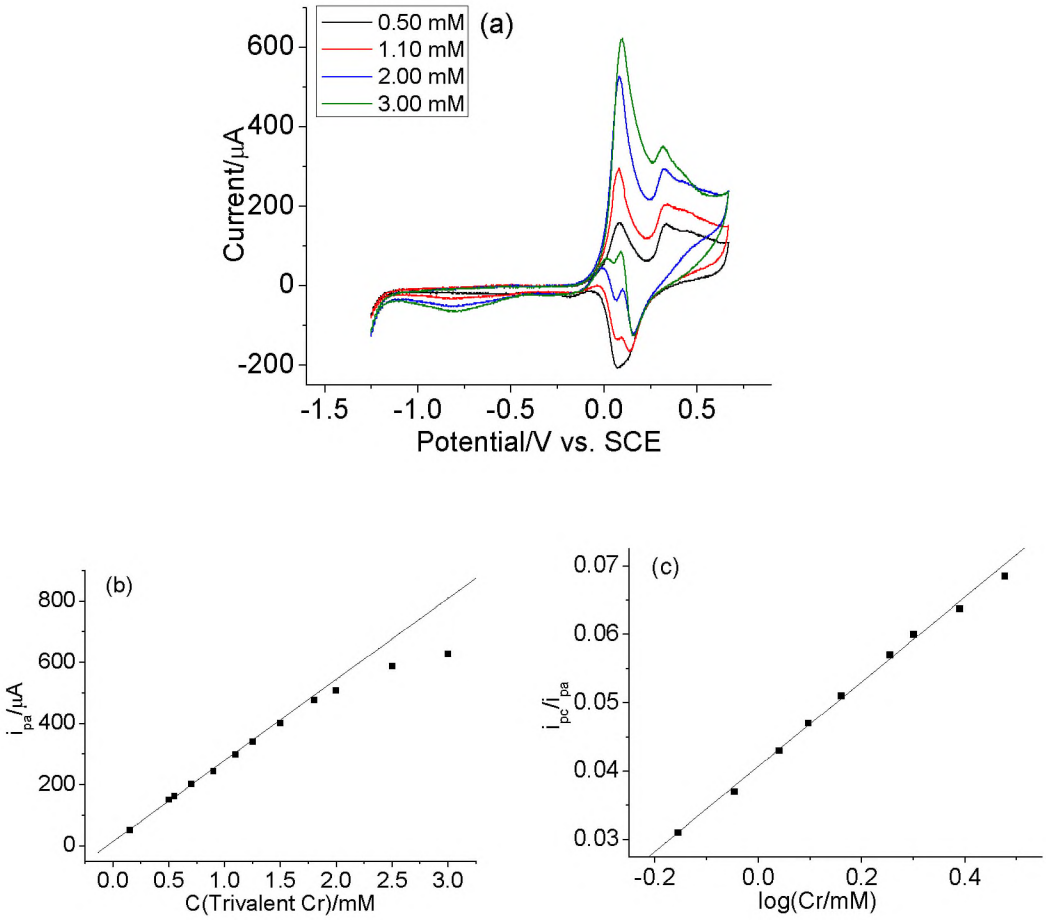

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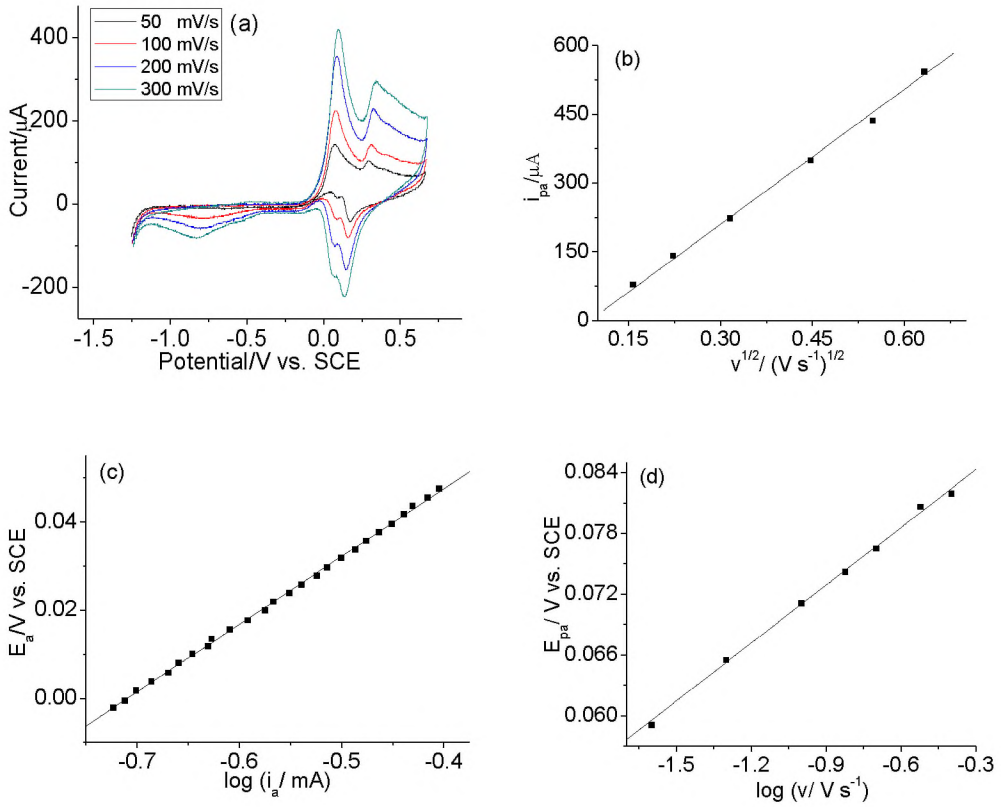

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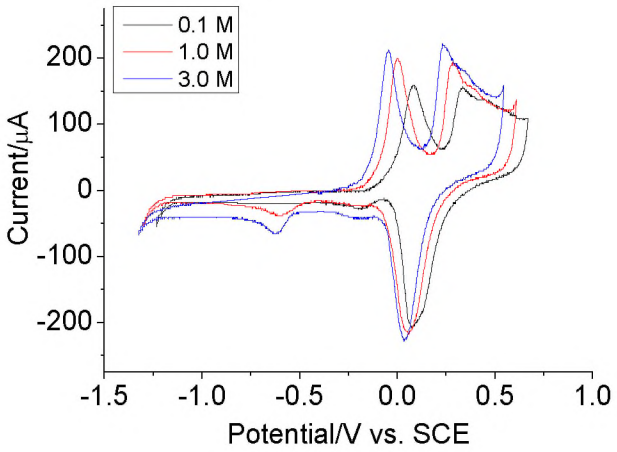

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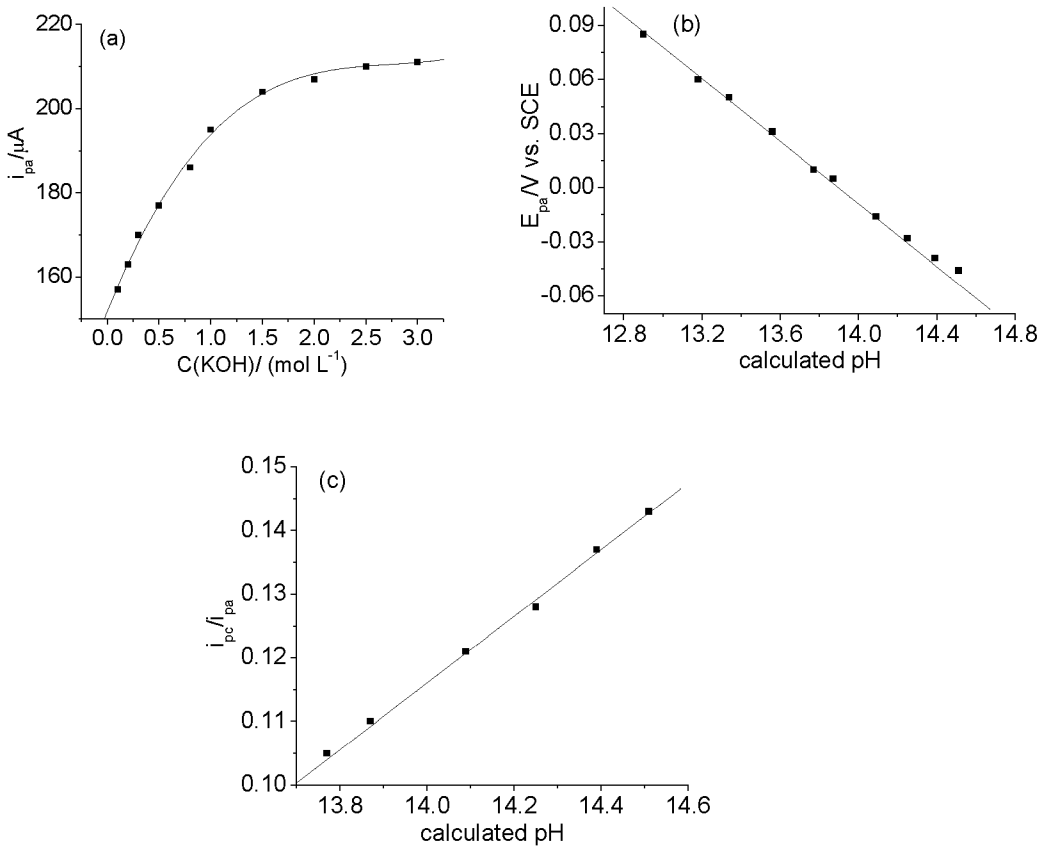

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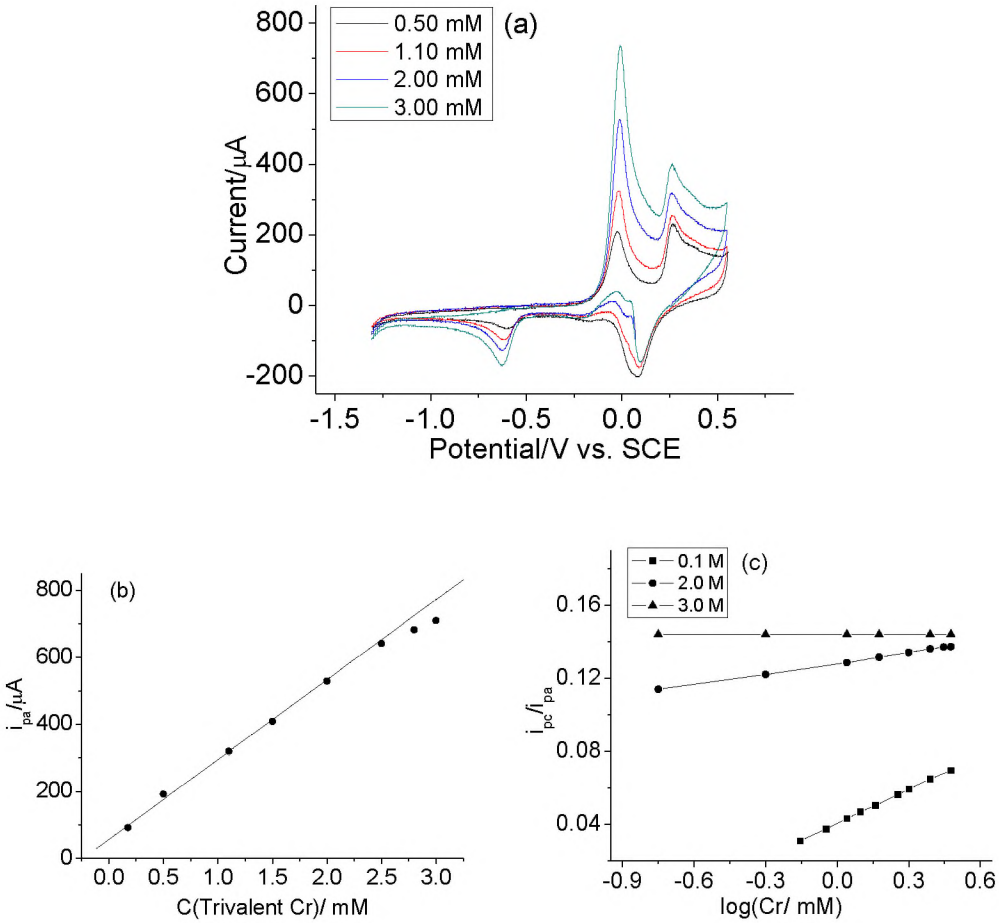

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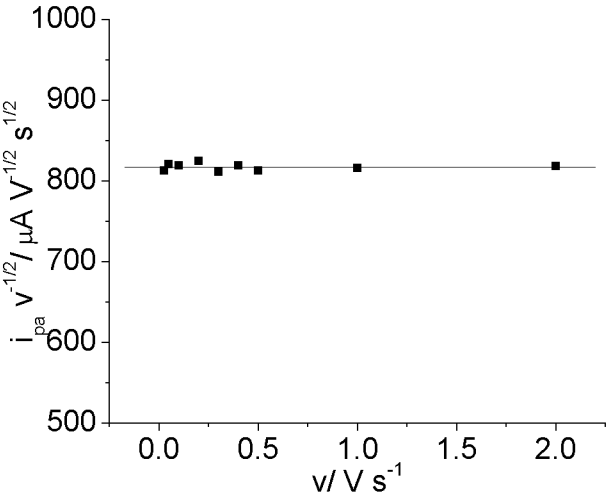

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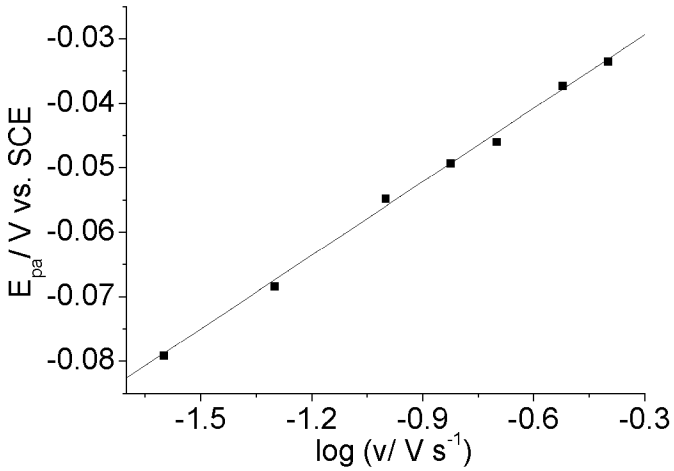

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